

# Absence of intermediate spin state in hole-doped $\text{LaCoO}_3$ : dynamical mean-field study

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The hole and electron doped  $\text{LaCoO}_3$  is studied using the dynamical mean-field theory. The one-particle spectra are analyzed and compared to the available experimental data, in particular the x-ray absorption spectra. Analyzing the temporal spin-spin correlation functions we find the atomic intermediate spin state is not important for the observed Curie-Weiss susceptibility. Contrary to commonly held view about the roles played by the  $t_{2g}$  and  $e_g$  electrons we find narrow quasi-particle bands of  $t_{2g}$  character crossing the Fermi level accompanied by strongly damped  $e_g$  excitations.

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Correlations arising from the electron-electron interaction within the narrow  $d$  bands put transition metal oxides among the most puzzling materials, properties of which may change substantially upon a small variation of temperature, pressure, carrier concentration or some other control parameter.  $\text{LaCoO}_3$  is a prominent example. A small gap non-magnetic insulator at low temperatures, its band structure is well described by an effective non-interacting electron picture.<sup>1</sup> Nevertheless, increased temperature or hole doping reveal its strongly correlated nature. Between 50 and 100 K the magnetic susceptibility sharply increases and acquires Curie-Weiss (CW) character, signaling the appearance of local magnetic moments.<sup>2</sup> The charge gap continuously disappears between 450 and 600 K accompanied by transfer of the optical spectral weight on several eV scale.<sup>3</sup> The generally accepted explanation is essentially atomic physics of the low spin ( $t_{2g}^6 e_g^0$ ) ground state with a nearby excited state of either high spin (HS,  $t_{2g}^4 e_g^2$ ) or intermediate spin (IS,  $t_{2g}^5 e_g^1$ ) character, where the precise nature of the excited state is not settled. The hole doping of the Co  $d$  bands due to substitution of La with Sr, Ca or Ba also leads to a strong magnetic response.<sup>4,5</sup> At < 18% Sr concentration microscopically inhomogeneous phase is observed that can be described as magnetic clusters separated by non-magnetic matrix characterized by insulating spin-glass behavior at low temperatures. Above 18% Sr concentrations the material becomes a homogeneous ferromagnetic (FM) metal. The transition between these two regimes, generally described as a percolation of the magnetic clusters, is associated with insulator-to-metal transition.

Properties of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  are commonly discussed in the context of double-exchange model which provides a satisfactory description of related  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  family. In this picture the  $t_{2g}$  electrons are localized on the metal atom forming the local spin moment while  $e_g$  electrons form dispersive bands. Numerous comparative studies, however, found sizeable differences between cobaltites and manganites. Colossal magnetoresistance, the hall-

mark of manganite physics, is not found in cobaltites.<sup>4,6</sup> The NMR relaxation rates in cobaltites are several orders of magnitude larger than in manganites.<sup>7</sup> The linear specific heat coefficient in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$  is 16 times larger than in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ .<sup>6</sup> These observations raise the question of the relevance of the double-exchange picture for doped cobaltites.

The strong  $T$ -dependence of physical properties even in the parent compound  $\text{LaCoO}_3$  make theoretical description of cobaltites challenging. Several density functional and Hartree-Fock calculations on doped cobaltites were reported,<sup>8–11</sup> which cannot treat dynamical electronic correlations. In this Letter we use the combination of the dynamical mean-field theory<sup>12</sup> and the density functional theory (DFT+DMFT)<sup>13,14</sup> to study the one-particle spectra and magnetic properties of doped  $\text{LaCoO}_3$ . Our results, which are relevant for doping  $x > 0.2$  with metallic FM ground state, contradict the double-exchange picture and the important role attributed to the IS atomic states. Our DMFT solution contains strongly damped local  $e_g$  excitations and dispersive  $t_{2g}$  bands crossing the Fermi level. We find that the local moments in doped cobaltites originate mostly in the HS state and give this statement quantitative meaning. We will argue that  $p-d$  covalency is necessary to explain the observed behavior.

The calculation proceeds in several steps. First, the LDA band structure is determined using WIEN2k<sup>15</sup> and an effective Hamiltonian spanning the Co  $d$  and O  $p$  bands is constructed.<sup>16,17</sup> For all dopings we used the same Hamiltonian obtained for the 5 K lattice parameters of the stoichiometric  $\text{LaCoO}_3$ . Adding the explicit electron-electron interaction within the Co  $d$  shell we arrive at the multi-band Hubbard Hamiltonian of the form

$$H = \sum_{\mathbf{k}} \begin{pmatrix} \mathbf{d}_{\mathbf{k}}^\dagger \\ \mathbf{p}_{\mathbf{k}}^\dagger \end{pmatrix} \begin{pmatrix} h_{\mathbf{k}}^{dd} - E_{\text{dc}} & h_{\mathbf{k}}^{dp} \\ h_{\mathbf{k}}^{pd} & h_{\mathbf{k}}^{pp} \end{pmatrix} \begin{pmatrix} \mathbf{d}_{\mathbf{k}} \\ \mathbf{p}_{\mathbf{k}} \end{pmatrix} + \sum_i W_i^{dd}. \quad (1)$$

Here,  $\mathbf{d}_{\mathbf{k}}$  ( $\mathbf{p}_{\mathbf{k}}$ ) is an operator-valued vector whose elements are Fourier transforms of  $d_{i\alpha}$  ( $p_{i\gamma}$ ), which anni-

hilate the Co  $d$  (O  $p$ ) electron in the orbital  $\alpha$  ( $\gamma$ ) in the  $i$ th unit cell. The on-site interaction  $W_i^{dd}$  is approximated by the density-density form for the sake of computational efficiency. The results of our previous study on  $\text{SrCoO}_3$ <sup>18</sup> justify this approximation. The interaction parameters  $U=6$  eV and  $J=0.8$  eV were taken from Ref. 19. The double-counting term  $E_{\text{dc}}$  approximately corrects for the explicitly unknown mean-field part of the interaction coming from LDA. It was chosen to equal the orbitally averaged Hartree part of the self-energy.<sup>20</sup> The hybridization expansion continuous-time quantum Monte Carlo<sup>21,22</sup> with the improved estimator for the self-energy<sup>23</sup> was used to solve the auxiliary impurity problem. Since the perturbation order is strongly imbalanced between weakly hybridized  $t_{2g}$  electrons and strongly hybridized  $e_g$  electrons, we use an improved measurement based on continuous-estimators to avoid poor statistics of the  $t_{2g}$  Green's function. All the real-axis spectra were obtained by direct analytic continuation of the self-energy using maximum entropy method.<sup>24</sup> The calculations were performed at the temperature of 580 K.

We start the presentation of our results with the analysis of local quantities in the non-spin-polarized state. The undoped system has the one-particle spectrum of a band insulator with a crystal-field gap between the filled  $t_{2g}$  and empty  $e_g$  states.<sup>19</sup> The  $p-d$  covalency leads to actual occupancies of the  $t_{2g}$  and  $e_g$  orbitals of 5.91 and 0.84, respectively. Fig. 1 shows the variation of the orbital occupancies with doping. The strong non-monotonicity indicates a departure from an independent particles behavior, in particular on the hole-doped side, where approximately two  $e_g$  electrons and three  $t_{2g}$  holes are created for each hole added to the system. This is accompanied by growing CW spin response as reflected in the local spin-spin correlation functions (right panel of Fig. 1). The competition between the different spin states of Co atom in  $\text{LaCoO}_3$  is sensitive to the relative positions of the Co  $d$  and O  $p$  bands as the  $p-e_g$  hybridization contributes substantially to the apparent crystal-field splitting. It is therefore crucial to establish that the present results do not depend on the variation of the double-counting correction  $E_{\text{dc}}$ , the definition of which is somewhat fuzzy in any DFT+ approach. In addition to the choice of self-consistently adjusted  $E_{\text{dc}}$ , used throughout the paper (see inset in Fig. 1), we have performed a series of test calculations with  $E_{\text{dc}}$  fixed to the value taken from the undoped system (stars in Fig. 1). Although the two values of  $E_{\text{dc}}$  differ as much as 1.3 eV at  $x=0.3$  we observe still the same behavior of the orbital occupancies.

Associating the CW response of an atom embedded in solid with a particular atomic multiplet may not be possible in a strongly hybridized and even metallic system. In Ref. 19 we have introduced the atomic state correlation matrix  $\Pi_{\alpha\beta} = \int_0^{1/T} d\tau \langle P_\alpha(\tau) P_\beta(0) \rangle$  to address this question in undoped  $\text{LaCoO}_3$ .  $\Pi_{\alpha\beta}$  includes effects of both quantum and statistical fluctuations and provides

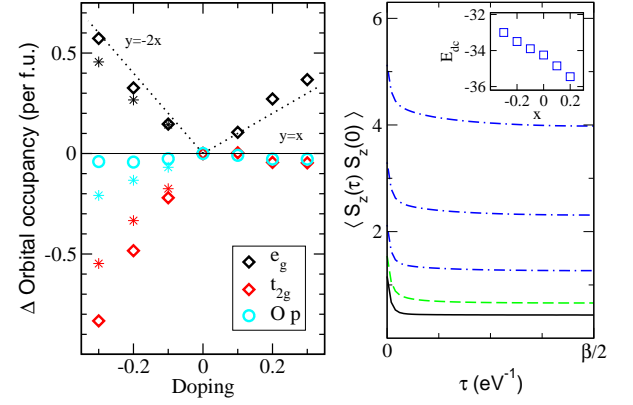


FIG. 1: (color online) Left panel: the doping dependence (hole doping  $< 0$ ) of the orbital occupancy. The stars mark results obtained with fixed double-counting correction. Right panel: the local spin-spin correlation functions: black (full line) – the undoped system, blue (dash-dotted line) – hole doping  $x=0.1, 0.2, 0.3$  (corresponding to increasing magnitude), and green (dashed line) – electron doping of 0.2. The inset shows the doping dependence of  $E_{\text{dc}}$ .

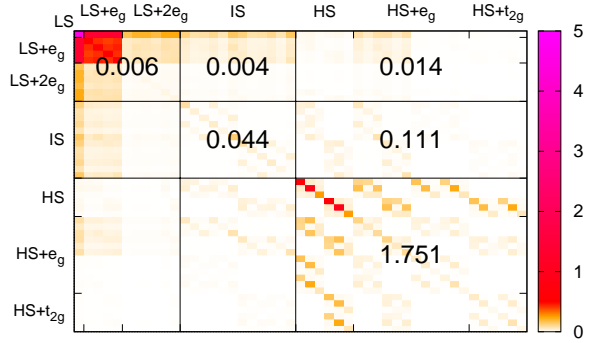


FIG. 2: Atomic state correlation matrix  $\Pi_{\alpha\beta}$  for the hole doping of  $x=0.2$  with the contribution of the most abundant  $d^6$ ,  $d^7$  and  $d^8$  states (see Ref. 19 for the notation). The numbers show the contributions to the local susceptibility  $T\chi_{\text{loc}}$  summed over the blocks.

information about the likelihood of finding the Co atom in state  $\alpha$  (column sum) as well as about the average duration of the visit to a given state (large diagonal elements mean long visits). Weighted with the spin matrix elements,  $S_\alpha^z S_\beta^z \Pi_{\alpha\beta}$  is the contribution of the pair  $\alpha\beta$  to the local susceptibility. The correlation matrix in Fig. 2 reveals that hole doping causes increasing weight of the HS block which dominates the local susceptibility, similar to the thermal effect in stoichiometric  $\text{LaCoO}_3$ .<sup>19,25</sup> This observation is consistent with our previous study on  $\text{SrCoO}_3$ .<sup>18</sup>

The one-particle spectral functions decomposed into their momentum and orbital contributions are shown in Fig. 3. The stoichiometric system exhibits sharp bands with well defined dispersion, reflecting the fact that an

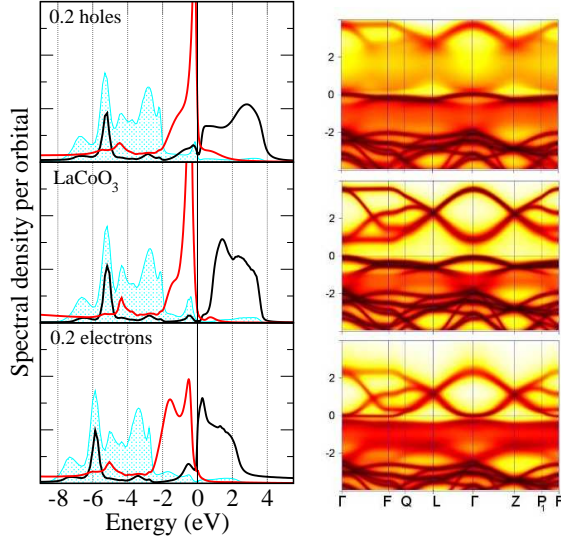


FIG. 3: (color online) Left panel: orbitally resolved spectral density: Co  $e_g$  (black), Co  $t_{2g}$  (red), O  $p$  (shaded blue),  $p - \pi$  (lighter blue) for various dopings. Right panel: the corresponding k-resolved spectral functions along the high symmetry lines in the Brillouin zone depicted as color plots.

additional  $e_g$  electron or  $t_{2g}$  hole behaves as a free particle. The electron doping introduces also some correlation effects, but we focus on the hole doping which is relevant for  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ . At  $x=0.1$  the chemical potential is pinned close to the top of the  $t_{2g}$  band (not shown). The  $e_g$  spectral weight is transferred from the coherent  $e_g - p$  anti-bonding band into incoherent structures around the chemical potential and fills the gap. With the number of holes growing the chemical potential shifts deeper into the  $t_{2g}$  band, which exhibits increasing mass renormalization. At higher doping levels some  $e_g$  spectral weight builds up at the chemical potential. These are strongly damped excitations with a lifetime 15 times shorter than that of  $t_{2g}$  excitations ( $-\text{Im} \Sigma_{e_g}(0) \approx 0.6$  eV,  $-\text{Im} \Sigma_{t_{2g}}(0) \approx 0.04$  eV). For the full evolution of the hole doped spectra up to  $x = 0.3$  see the Supplemental Material.<sup>26</sup>

The overall shape of the O  $p$  spectrum is unaffected by doping. In particular, the positions of the non-bonding ( $\sim -3$  eV) and the  $\sigma$ -bonding peaks ( $\sim -5.5$  eV) remain unchanged. This compares well with the photoemission data of Saitoh *et al.*,<sup>27</sup> where the peaks shift as little as 0.4 eV between  $x = 0$  and  $x = 0.4$ , and *a posteriori* justifies our choice of the double-counting correction. The calculated as well as the experimental electron-removal (photoemission) spectra exhibit only a minor variation with the hole doping. The electron-addition spectrum experiences more pronounced changes. These can be measured by means of the x-ray absorption spectroscopy. Small core-hole effects in the oxygen K-edge spectrum allow a direct comparison of the XAS data with the O  $p$  spectral function. In Fig. 4 we show the evolution of the positive energy part of the O  $p$  spectra broadened

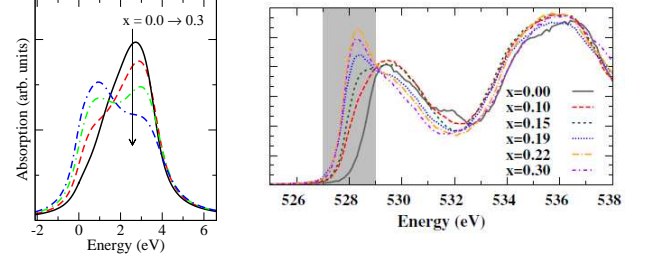


FIG. 4: Left: the unoccupied O  $p$  spectra (broadened with Lorentzian) for various dopings. Right: The experimental XAS spectra reproduced from Ref. 10.

to account for XAS linewidth. The observed transfer of spectral weight is driven by the corresponding evolution of the Co  $e_g$  spectrum. Our spectra provide a good description of the recent experimental observations of Medling *et al.*<sup>10</sup> In the LSDA theory used by Medling *et al.* the hole doping shifts the chemical potential deeper into the  $t_{2g}$  peak while the bandstructure remains essentially rigid. As a result some O  $p$  states are brought above the chemical potential, due to hybridization with the Co  $t_{2g}$ 's, leading to the increase of the lower energy peak. The peak at higher energy, coming from  $e_g - p$  hybridization is unaffected by doping in the theory of Medling *et al.* This is at odds with the experimental data, which show an increase of the low-energy peak with a simultaneous decrease of the high-energy one, accompanied by appearance of an isosbestic point.<sup>28</sup> The spectral densities obtained with the present theory in Fig. 4 exhibit precisely this behavior. The increase of the low-energy peak in our data arises partly from the depopulation of the  $t_{2g}$  states and partly from the incoherent  $e_g$  excitations, which gradually fill the gap in  $\text{LaCoO}_3$  spectrum. Decrease of the high-energy peak in Fig. 4 follows the diminishing weight of the  $e_g$  anti-bonding peak.

For the hole doping  $x = 0.3$  there is a stable FM solution at  $T=580$  K. The ordered moment of  $1.2 \mu_B$  per formula unit is close to saturation as was confirmed by calculation at lower temperature. The spectral functions are shown in Fig. 5. There is a clear similarity between this spectrum and the spectrum calculated for  $\text{SrCoO}_3$ .<sup>18</sup> In particular, the majority  $t_{2g}$  and minority  $e_g$  states are absent from the chemical potential, while the minority  $t_{2g}$  states form a well defined band, which is the main conduction channel. The majority  $e_g$  states form a strongly damped band which crosses the chemical potential. The spin-averaged spectra exhibit only minor difference to the PM spectra, while the  $e_g$  lifetime is by a factor of two larger in the FM phase.<sup>26</sup> The atomic state correlation matrices show no sizable redistribution of the multiplet weights, in particular no enhancement of the IS block, due to the spin polarization. This shows that inter-site FM correlations, which are completely absent in the PM solution, do not stabilize the IS state.

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  is commonly compared to perovskite manganites and the double-exchange model is invoked



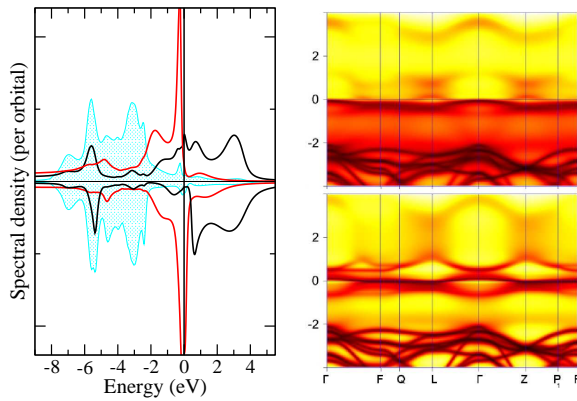


FIG. 5: (color online) Left panel: orbitaly resolved spectral density: Co  $e_g$  (black), Co  $t_{2g}$  (red), O  $p$  (shaded blue),  $p - \pi$  (lighter blue) for the ferromagnetic solution obtained at  $T=580$  K and hole doping  $x=0.3$ . (Minority spin densities are multiplied with  $-1$ ). Right panel: The corresponding  $k$ -resolved spectra for the majority (top) and minority (bottom) polarization.

with the partially populated  $e_g$  band providing the conduction channel. In this setting the  $d^6$  IS state is a natural building block maximizing the kinetic energy gain. Our results provide a picture, which differs in two important aspects: (i) the HS state is identified as the major contributor to the CW susceptibility, (ii)  $t_{2g}$  quasiparticles are found at the Fermi level while the  $e_g$  excitations are strongly damped. In the rest of the paper we discuss our results in the light of the known experimental data.

First, the computed saturated FM moment at  $x = 0.3$  is  $1.2 \mu_B$  per formula unit, slightly below the experimental value,<sup>4,29</sup> although our analysis shows that it originates largely from the HS state, i.e. the saturation magnetization is not a good indicator for the underlying multiplet dynamics. Second, we studied only homogeneous solutions with full crystal periodicity. The results are, therefore, not relevant for the spin-state polaron regime at very low doping.<sup>30,31</sup> It is plausible that while IS states participate in the polaron formation they are not important at higher doping levels. The polaron is stable if the kinetic energy gain from delocalizing an  $e_g$  electron over the polaron volume outweighs the cost of exciting the participating atoms into the IS state. While the latter term grows linearly with the size of the polaron, the kinetic energy gain is largest for small polarons and quickly saturates as the polaron grows. Therefore only small polarons are stable and a substantial change of magnetic properties around  $x = 0.05$ <sup>32</sup> suggests that quite different microscopic physics is involved.

The other arguments against the IS state in the metallic phase ( $x > 0.2$ ) are the lack of substantial magnetoresistance (found in manganites),<sup>6</sup> no Griffiths phase,<sup>33</sup> and observation of positive curvature of inverse susceptibility above  $T_c$ .<sup>33</sup> The last observation points to increase of the paramagnetic moment with temperature, while in

the IS scenario one would expect decrease of IS atoms in magnetically disordered phase. Instead of the double-exchange mechanism stabilizing the spin-state polarons, which relies on the spin polarization on nano-scale, we attribute the population of HS state to the following covalency effect. Introducing a hole on Co atom is likened to substitution of a more electronegative atom in the Co lattice, which is known to induce the HS state on its neighbors<sup>34,35</sup> due to reduction of the hybridization part of the crystal field. Self-consistent adjustment of the system to this situation establishes a new balance of  $t_{2g}$  holes and  $e_g$  electrons.

The second, and perhaps most important, result of the present study is the observation of much stronger damping of  $e_g$  excitations than their  $t_{2g}$  counterparts. To provide a qualitative explanation of this effect we make the following observations. First, the effect is still present in spin-polarized solution, which is easier to analyze since the occupied majority  $t_{2g}$  and empty minority  $e_g$  orbitals do not play active role. Second, we found a similar effect in a simplified two-band model of Ref. 36 when hole doped. The situation can be viewed as two partially filled asymmetric bands of spinless fermions. The second Born approximation for the self-energy in the imaginary time

$$\Sigma_\sigma(\tau) = U^2 G_\sigma(\tau) G_{-\sigma}(\tau) G_{-\sigma}(\beta - \tau), \quad (2)$$

where  $\sigma = \pm 1$  indexes the two bands, shows that the ratio of the self-energies at  $\beta/2$  is the inverse ratio of the Green functions. This approximately means that the band with lower density at the Fermi level has more strongly damped quasiparticles. In other words, the slow  $t_{2g}$  holes act as ‘static’ scattering centers for the fast  $e_g$  electrons, while the  $t_{2g}$  holes perceive the  $e_g$  electrons as ‘homogeneous gas’. Although calculation of the transport coefficients is beyond the scope of this study we make several speculative comments. The present solution is consistent with the absence of colossal magnetoresistance. The anomalous Hall effect observed in FM metallic phase<sup>29</sup> may be related to the spin-orbit effects in the  $t_{2g}$  quasiparticle band crossing the Fermi level. Finally, the contribution of both  $t_{2g}$  and  $e_g$  channels with different quasiparticle dampings, of which the  $e_g$  one is more sensitive to the magnetic order, should be considered when interpreting the  $T$ -dependence of thermopower.<sup>37</sup>

In summary, we have used dynamical mean-field theory to investigate hole doped  $\text{LaCoO}_3$ . Our results provide a good description of the spectral and magnetic properties of the homogeneous metallic phase for  $x > 0.2$ . We have found that IS state does not play important role in this regime and that the CW susceptibility can be attributed to HS state and fluctuation around it. We found coherent  $t_{2g}$  band crossing the Fermi level, while the  $e_g$  excitations are strongly damped and appear at the Fermi level only at dopings  $x > 0.2$ . This leads to the conclusion that double-exchange model with  $e_g$  band as the only conduction channel is not appropriate for doped cobaltites.

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